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POLARIZATION STABILITY OF AMORPHOUS PIEZOELECTRIC POLYIMIDES

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Abstract. Amorphous polyimides containing polar functional groups have been synthesized and investigated for potential use as high temperature piezoelectric sensors. The thermal stability of the piezoelectric effect of one polyimide was evaluated as a function of various curing and poling conditions under dynamic and static thermal stimuli. First, the polymer samples were thermally cycled under strain by systematically increasing the maximum temperature from 50°C to 200°C while the piezoelectric strain coefficient was being measured. Second, the samples were isothermally aged at an elevated temperature in air, and the isothermal decay of the remanent polarization was measured at room temperature as a function of time. Both conventional and corona poling methods were evaluated. This material exhibited good thermal stability of the piezoelectric properties up to 100°C.

Key words. amorphous polyimides, piezoelectricity, thermal stability, temporal stability, corona poling, partial curing

Subject classification. Physical Sciences: Materials

1. Introduction. Aromatic polyimides have been used in a wide variety of aerospace applications because of their chemical and radiation resistance, with excellent thermal, mechanical, and dielectric properties. Recently, a series of novel piezoelectric polyimides containing pendant, polar groups have been synthesized and evaluated at NASA-LaRC for potential use in micro-electro-mechanical systems (MEMS) devices [1,2]. The initial investigations have shown that they exhibited a piezoelectric response at temperatures in excess of 150°C [3]. Experimental studies of the thermal stability of a piezoelectric amorphous polyimide, (β -CN)APB/ODPA, are presented here as a function of various curing and poling conditions under dynamic and static thermal stimuli. Both conventional and corona poling methods were employed for this study. Corona poling was used to maximize the degree of dipolar orientation and minimize localized arcing during in-situ imidization and poling. The results of both poling methods are discussed.

2. Experimental

2.1. Film preparation. The polyimide evaluated was (β -CN)APB/ODPA, which was prepared from 2,6-bis(3-aminophenoxy) benzonitrile ((β -CN)APB) and 4,4' oxidiphthalic anhydride (ODPA) via a polyamic acid solution in N,N-dimethylacetamide and subsequent thermal imidization. The synthesis was reported in detail elsewhere [3]. The polyamic acid solution was cast to form approximately 30 μ m thick films. The tack-free films were imidized under various cure cycles to produce samples having different degrees of imidization. The exact cure cycles are summarized in Table 1. A silver layer, approximately

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200nm thick, was evaporated on both sides of the films for conventional poling and only one side of the films for corona poling.

TABLE 1.

Processing parameters and properties of partially cured, corona poled (β -CN)APB/ODPA: cure cycle, T_g , degree of imidization ($A_{1780\text{cm}^{-1}}/A_{1500\text{cm}^{-1}}$), and P_r .

| Sample | Cure cycle ($^{\circ}\text{C}$) 1 hour each, N_2 | T_g before poling ($^{\circ}\text{C}$) | $A_{1780\text{cm}^{-1}}/A_{1500\text{cm}^{-1}}$ | P_r (mC/m^2) |
|--------|--|---|---|-------------------------------------|
| P100 | 50, 100 | 97 | 0.18 | N/A |
| P150 | 50, 150 | 142 | 0.69 | 26 |
| P200 | 50, 150, 200 | 166 | 0.82 | 9 |
| P240 | 50, 150, 200, 240 | 218 | 1.00 | 4 |

2.2. Poling. The film specimens were poled using either a conventional or a positive corona poling procedure. For the conventional poling, each sample was polarized by the application of a DC electric field (80MV/m) at an elevated temperature ($T_g + 5^{\circ}\text{C}$) in a silicone oil bath. For corona poling, a DC field of 20 kV was applied to generate a positive corona using a single tungsten wire for four hours at 223°C and one hour at 212°C . The distance between the corona tip and the specimen was approximately 30mm. An argon gas was maintained during the poling process. For both poling processes, the dipoles were oriented with the applied field at a temperature above T_g , with subsequent cooling to below T_g in the presence of the applied field. The resulting remanent polarization (P_r) is directly proportional to the material's piezoelectric response, and estimated from the following equation [4],

$$P_r = \epsilon_0 \Delta\epsilon E_p \quad (1)$$

where ϵ_0 is the permittivity of free space (8.854 pF/m), $\Delta\epsilon$ is the dielectric relaxation strength, and E_p is the poling field.

2.3. Characterization.

2.3.1. Degree of imidization. The glass transition temperatures (T_g) of the films were measured by differential scanning calorimetry using a Shimadzu DSC-50 at a heating rate of $20^{\circ}\text{C}/\text{min}$ in air. The T_g was taken as an inflection point of the shift of the baseline of the DSC thermogram. The degree of imidization was determined by a Nicolet FTIR spectrometer in an ATR mode using a Nicolet Contin`m IR microscope. The absorption peak at 1780cm^{-1} (sym. carbonyl stretch) was used to determine the degree of imidization and that at 1500cm^{-1} (ring breathing modes of the aromatic moieties) was used as an internal standard [5]. The results are presented in Table 1.

2.3.2. Thermally stimulated current (TSC) measurement. After poling, P_r was measured as a function of temperature. As the sample was heated through its T_g at a heating rate of $1.5^{\circ}\text{C}/\text{min}$, the depolarization current was measured using a Keithly 6517 electrometer. The P_r is equal to the charge per unit area, which is obtained from the data by integrating the current with respect to time and plotting it as a function of temperature.

2.3.3. Piezoelectric measurement. The piezoelectric strain coefficient (d_{31}) was measured using a Rheovibron DDV-II-C mechanical analyzer as a function of temperature for a range of frequencies. As

the polymer is strained along the direction of applied stress, a charge Q is generated on the surface of the electrodes. A geometric factor is used to produce a geometry independent parameter, namely, surface charge density per unit applied stress.

2.3.4. Thermal stability measurements. Thermal stability of the piezoelectricity in the (β -CN) APB/ODPA system was carried out under both dynamic and isothermal conditions. First, the polymer sample was thermally cycled under strain by systematically increasing the maximum temperature from 50 to 200°C at a heating rate of 2°C/min. The d_{31} was measured as a function of temperature for four runs, where the maximum temperature for each run was 50, 100, 150°C and 200°C. The effect of the dynamic temperature cycling on the d_{31} was assessed as % retention of the piezoelectric response. Second, the as-poled samples were isothermally aged at 50, 100, 150 and 200°C in static air ovens. The aged samples at each temperature were tested periodically and the P_r was measured and compared to that of the as-poled sample. The % retention of P_r was plotted as a function of aging temperature and time.

3. Results

3.1. Fully cured, conventionally poled (β -CN)APB/ODPA. The remanent polarization of the fully cured, conventionally poled (β -CN)APB/ODPA was approximately 20mC/m² when poled at 80MV/m for one hour above T_g . Figure 1 summarizes the results of the long-term thermal stability of this polymer. The retained P_r after isothermal aging is presented as a function of aging time at the various temperatures. Excellent thermal stability was observed up to 100°C, and no loss of the piezoelectric response was seen after aging at 50°C and 100°C up to 500 hrs. After aging at 150°C, 50% of the initial P_r was retained after 100 hrs, and remained constant until 450 hrs, while at 200°C, 13% of the P_r was retained after 100 hrs.

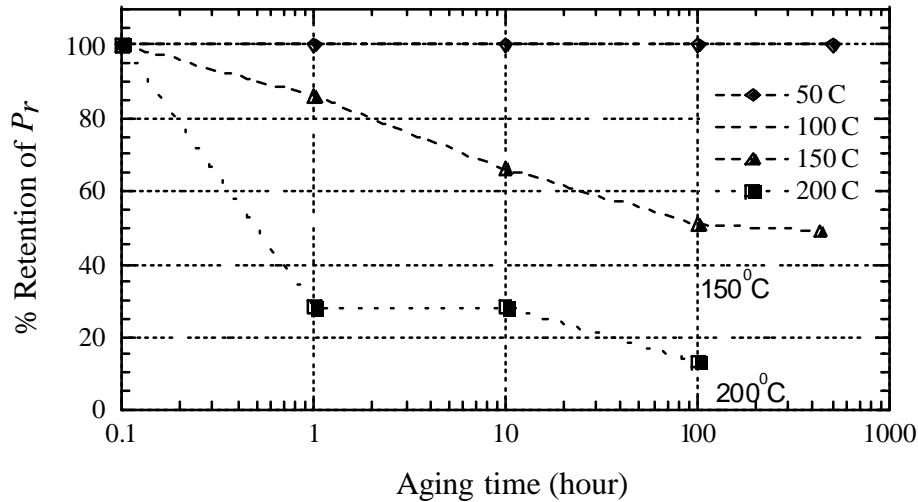


FIG. 1. Thermal stability of P_r of (β -CN)APB/ODPA after aging at various temperatures.

Thermal stability of the piezoelectric strain coefficient (d_{31}) under dynamic conditions was also studied and the results are shown in Figure 2. After cycling up to 50°C, no loss of the initial d_{31} was observed on the 2nd run, as seen in the inset of Figure 2. The d_{31} of this polymer rapidly increased with

temperature above 90°C. A d_{31} value of 5pC/N at the end of the 3rd run at 150°C and that of 10pC/N at 200°C at the end of the 4th run were obtained. These results are encouraging and portend use of these polyimides as sensors in high temperature aerospace applications.

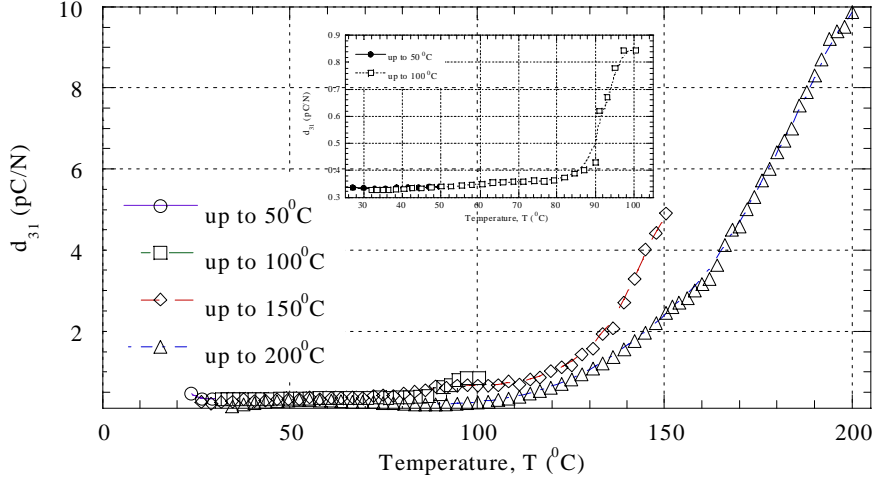


FIG. 2. *Dynamic stability of d_{31} of fully cured, conventionally poled polyimide film (1 Hz).*

3.2. Partially cured, corona poled (β -CN)APB/ODPA. A positive corona poling was used for the partially cured polymers in an attempt to maximize the degree of dipolar orientation and minimize localized arcing during in-situ imidization and poling. The aligned polar groups should be immobilized by additional imidization and subsequent cooling in the presence of an electric field. Table 1 summarizes the cure cycle, T_g , and degree of imidization of the polyimides. Both the T_g and the degree of imidization increased almost linearly with the final cure temperature. Thus, higher mobility of the dipoles should be expected for the polymers cured at a lower temperature. The remanent polarization of these specimens was measured, and listed in Table 1. The value of P_r appeared higher when cured at lower temperature. Since the mobility of the molecules of the partially cured polyimide should be much higher than that of the fully cured one, the polar groups of the former are expected to orient parallel to the field direction more efficiently than the latter. Therefore, poling in a partially imidized state may produce a higher degree of dipole orientation than poling in a fully imidized state, thereby generating higher P_r . The P150 partially cured polyimide exhibited six times higher P_r than the fully cured one under the same corona poling condition, which was greater than expected from the preliminary dielectric measurement. Figure 3 shows an example of the P_r of a partially cured, corona poled (β -CN) APB/ODPA (P150). The partially cured polymers tend to show broad double depolarizing current peaks during TSC measurement while the fully cured ones depolarize with one sharp peak near T_g . The double peaks imply incomplete imidization during poling since the peak represent the T_g and the dipoles poled in a partially imidized state are thermally less stable than those poled in a fully imidized state. Since the poling temperature for the partially cured polymers was selected 5°C above T_g of the fully cured one, the dipoles aligned in the early stage (unimidized state) may not have had enough time to relax their excessive free volume during the in-situ imidization and poling process. A gradual increase of the poling

temperature may be desirable to shift the lower peak maximum to the higher temperature, providing more thermal stability to the polarized dipoles.

Figures 4(a) and (b) show the normalized retention of the piezoelectric strain coefficient, d_{31} of the dynamic stability tests for both fully cured, conventionally poled and the partially cured, corona poled (β -CN)APB/ODPA (P150), respectively. In both cases, the films exhibit very good thermal stability and

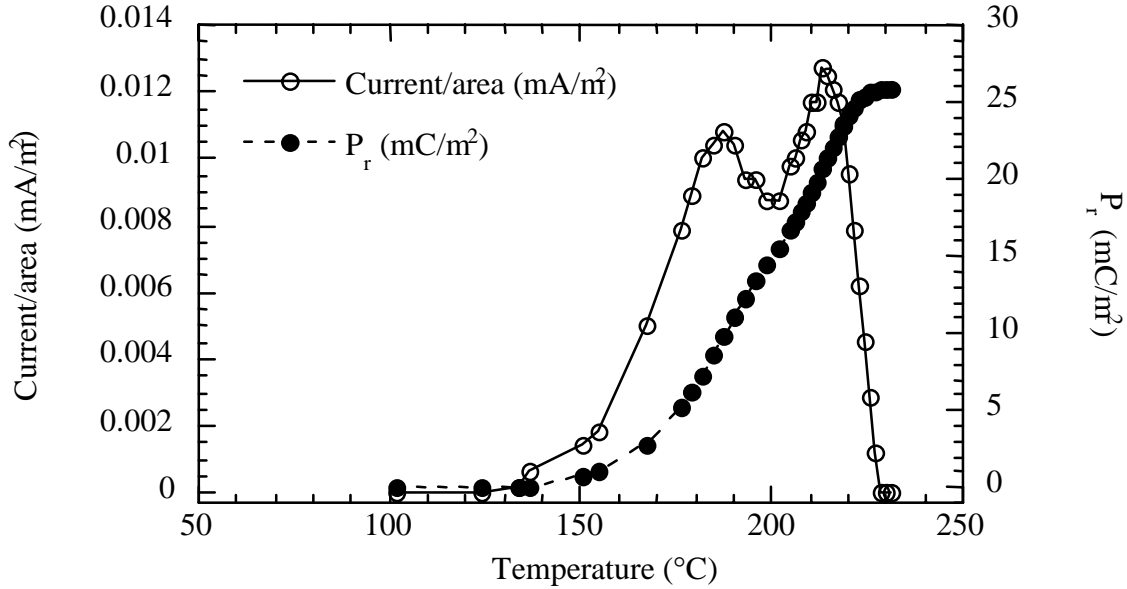


FIG. 3. Thermally stimulated current measurement: current/area and P_r versus temperature for partially cured (β -CN) APB/ODPA (P150).

virtually no loss of d_{31} was observed prior to reaching 150°C. After 150°C, both films exhibited noticeable loss of d_{31} , however, the fully cured specimen still retained about 60% of the initial value while the partially cured one retained less than 20%. The lower value of the partially cured one may be an artifact due in part to incomplete imidization (Figure 3). Further investigations in this matter are underway. The thermal stability of the poled amorphous polyimide films did not show a significant change in the range of the measurement frequencies, from 1Hz to 100Hz for both poling processes.

4. Conclusions. Thermal stability of the amorphous piezoelectric polyimide was evaluated as a function of curing and poling conditions. The piezoelectricity of this polymer was stable under both dynamic and static thermal stimuli and statistically no loss was observed up to 100°C. The partially cured, corona poled polymers exhibited improved remanent polarization. Since this amorphous piezoelectric polyimide can generate a piezoelectric response at elevated temperatures, its thermal stability should be beneficial for high temperature aerospace applications.

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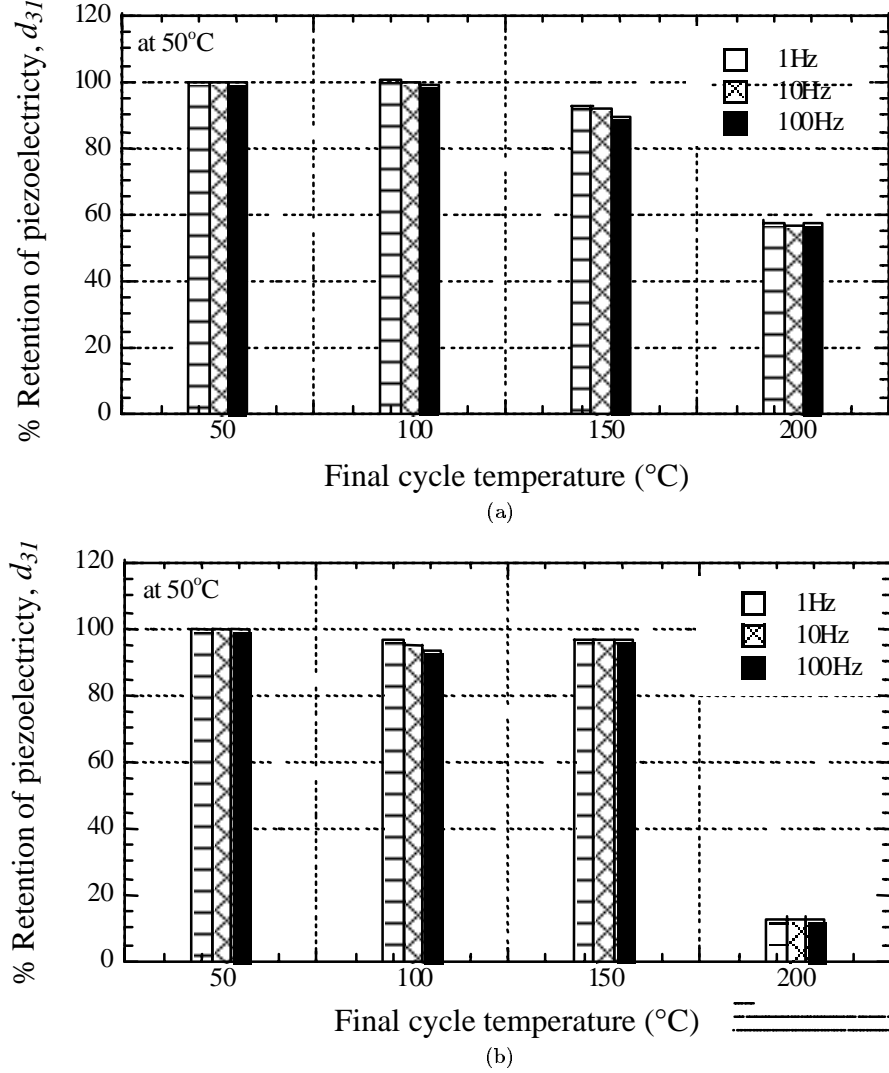


FIG. 4. Percent retention of the piezoelectric strain coefficient, d_{31} at 50°C after cycling up to 50, 100, 150, and 200°C, (a) fully cured sample (conventional poling: 80MV/m, 220°C for 60min), (b) partially cured sample (corona poling).

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